A STUDY OF THE EFFECT OF BORINES ON THE FORMATION OF ADDITION POLYMERS

BY

ARCH BYRON SPRADLING, JR.

A. B., Grinnell College, 1940
M. S., University of Illinois, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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OF ILLINOIS, 1944

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Acknowledgment

The author wishes to express his sincere appreciation for the suggestions and guidance given him by Dr. H. R. Snyder in the undertaking of this work.

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Introduction

The use of borines as catalysts for initiating certain polymerizations has been reported previously.[1] In view of the similarity between borines and boron fluoride, whose catalytic power is believed to be due to its ability to form coordination complexes with monomer molecules, it might be expected that borines would catalyze the polymerization of vinyl monomers by an ionic process. However, since borines are exceptionally reactive toward molecular oxygen, the possibility exists that polymerizations in their presence actually are initiated by free radicals formed by the action of traces of oxygen on the borines. The present work was undertaken to investigate further polymerizations catalyzed by borines and to elucidate the mechanism of the reactions.

Discussion

Numerous polymerizations of unsaturated compounds were performed in the presence of tri-*t*-butyl borine; they were conducted in bulk, solution, and emulsion. The quantity of borine used varied from 0.02 to 2.0 percent by volume of the monomer. Vinyl acetate, methyl acrylate, acrylonitrile, vinyl chloride, and styrene yielded high polymers, but attempts to polymerize butadiene, isoprene, β-pinene, pentene-1, and pentene-2 were unsuccessful. It was found that when polymerizations were attempted in bulk, vinyl acetate polymerized readily, but the polymerization of styrene proceeded very slowly; however, attempts to polymerize vinyl acetate in emulsion were unsuccessful although styrene formed high polymers under these conditions. With monomers other than styrene and vinyl acetate parallel results were obtained in bulk and emulsion polymerizations.

In general polymerizations were conducted in an atmosphere of nitrogen although air and oxygen were employed in certain experiments. Molecular weight determinations showed that for polymers formed in an atmosphere of nitrogen the molecular weight increased with decreasing catalyst concentration. The presence of small amounts of oxygen during polymerization increased the molecular weight and also the yield of the polymer. An atmosphere of pure oxygen prevented polymerization of some monomers.

Evidence for a mechanism of the polymerization in the presence of borines was obtained. It has been postulated that the autooxidation of a borine proceeds by way of an intermediate borine peroxide.[2] It is believed that an active fragment resulting from the decomposition of the borine peroxide initiates polymerization and that it proceeds by a free radical mechanism. Both the starch-iodide and the ferric thiocyanate tests indicated that borines form stable peroxides, for positive tests were obtained as long as seventy-two hours after an aqueous suspension of tri-*t*-butyl borine was placed in contact with air. A kinetic study of the polymerization of *l*-menthyl acrylate showed that the presence of oxygen is essential for polymerization. Attempts to initiate polymerizations with tri-α-naphthyl borine were unsuccessful. Since tri-α-naphthyl borine is not sensitive to oxygen, these results indicate that the borine-catalyzed polymerizations proceed by a free radical mechanism.

A study of the effect of various compounds as inhibitors was undertaken. Hydroquinone had little retarding effect on the polymerization of vinyl acetate by tri-*t*-butyl borine, but pyrogallol prevented the reaction. Sulfur likewise prevented polymerization, and amines exhibited various degrees of activity as inhibitors. The most effective of the amines tested was phenyl-β-naphthylamine. Picric acid, nitrobenzene, and trinitrobenzene also greatly retarded polymerization, but trinitrobenzene was less effective than nitrobenzene.

Since borines form stable peroxides, these compounds should influence reactions which are sensitive to peroxides. However,

attempts to reverse the mode of addition of hydrogen bromide to styrene and isobutylene by means of tri-*t*-butyl borine in the presence of air were unsuccessful.

Bibliography

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[2] Johnson and Van Campen, J. Am. Chem. Soc., **60**, 121 (1938).

Vita

The author was born in St. Louis, Missouri, on May 22, 1918. He attended the public schools of Webster Groves, Missouri, and was graduated from Webster Groves High School in 1936. In September, 1936, he entered Grinnell College and was granted the degree of Bachelor of Arts in June, 1940. In September, 1940, he entered the Graduate School of the University of Illinois and was granted the degree of Master of Science in June, 1942. During the years 1940-1944 he held an Assistantship in Chemistry.

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